

^{14}C and ^{13}C Isotopic Composition of Methane Dissolved in Porewaters and Groundwaters and Emitted from Red Lake, Minnesota peatlands

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The isotopic composition of methane dissolved in porewaters and groundwaters and emitted from the surface of peatlands of the Red Lakes District, Minnesota, was characterized. Groundwater collected from 100 foot deep wells contained methane at concentrations as high as 0.4 to 1.6mM (5 wells) while most wells (12) contained below 1 μM methane. Methane recovered from the wells with the higher concentrations was biogenic ($\text{C}_1/\text{C}_2 > 10,000$; $\delta^{13}\text{C}$ -70 to -95‰, δD -298 to 312‰) but radiocarbon dead (apparent age >40,000 years, $\Delta^{14}\text{C}$ -995 to -1000‰). This methane apparently formed biogenically long ago and has been sequestered, or it formed from ancient organic matter. Methane extracted from porewaters recovered from the peat column yielded apparent ages (^{14}C) of modern to 500 years ($\Delta^{14}\text{C}$ 23 to -68‰) in surface intervals (0.5 to 1m) increasing to 1500 to 3000 years ($\Delta^{14}\text{C}$ -176 to -305‰) at depths of 2.5 to 3 meters. the $\delta^{13}\text{C}$ of porewater methane ranged from -61 to -88‰ while δD was from -260 to -300‰. Methane collected at the sediment surface was generally ^{13}C enriched relative to deeper methane (-48 to -60‰) but δD values were lighter or similar to deeper porewater methane (-265 to -329), so surficial methane oxidation was not clearly indicated. Emitted methane was always modern ($\Delta^{14}\text{C}$ +118 to 152‰) and $\delta^{13}\text{C}$ ranged from -60 to -75‰.

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